Propane Recovery Project Overview
Aug 13 2012

Phillips 66
San Francisco Refinery

PRP - Coker Fuel Gas Hydrotreater scope

New Coker Fuel Gas Hydrotreater to remove mercaptan sulfur

- Coker Propane / Butane contains contaminates (Olefins / Mercaptan Sulfur)
- Hydrotreating will remove contaminates. Refinery fuel gas TRS will be reduced by 75 %. Approx. 0.75 TPD reduction in refinery SOx emissions
- Fuel Gas feed streams contain sufficient Hydrogen for treating reaction
- Re-use existing Hydrogen Plant Feed Compressor
- Re-use existing Hydrogen Plant feed system Hydrotreating Reactors
- Operate reactors around 280 PSI and 500 F
- Coker Fuel Gas Mercaptan Sulfur removal increases refinery Sulfur Plant load by less than 2 %
- Located on the site of an existing Hydrogen Plant

BAY AREA
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Petroleum Refinery Emissions Reduction Strategy:

Initial Report

Prepared by the staff of the
Bay Area Air Quality Management District

May 2015

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Rule Development / Public Consultation Process

During this multi-phased rule development effort staff will strive to engage all interested stakeholders, including affected industry, nearby community members, environmental organizations, other governmental agencies, the media, and other interested parties. There are several aspects to this public engagement, including:

- Development of conceptual versions of draft rules with discussions of those concepts;
- Scheduling and siting of public workshops (which will be held in and around communities impacted by refinery emissions) with the timely release of associated draft regulatory language, preliminary reports, and support documents;
- Meetings and consultations (community meetings, phone conversations, emails, letters) with interested stakeholders in less formal settings to discuss concerns and issues;
- Preparation of a regulatory package for the consideration of the Air District Board of Directors, including:
    - Proposed regulatory language;
    - A Staff Report presenting the staff's findings, such as descriptions of the refining industry, regulatory history, summary and explanation of the proposal, emissions and emission reductions estimates, costs, cost effectiveness and incremental cost effectiveness, environmental and socioeconomic impacts, a schedule of implementation (when the provisions of the rule become effective if adopted), and staff recommendations to the Board of Directors;
    - An environmental analysis report;
    - A socioeconomic analysis report;
    - A discussion of and responses to comments received on the proposed rule, staff report, and environmental and socioeconomic analyses;
- Public Hearing, where the staff's presentation is made and stakeholders may provide testimony to the Board of Directors on the staff proposal and at which the Board would consider the adoption of the proposal.

Schedule of Refinery Strategy Regulatory Development

The following table provides a preliminary schedule for the development of each of the three phases of the regulatory effort. It should be noted that these are only rough estimates of the schedule and the dates may change as the effort proceeds.

Milestone	Phase 1	Phase 2	Phase 3
Concepts	April 2015	April 2015	3rd Quarter 2015
Workshops	2nd Quarter 2015	2nd Quarter 2015	2nd Half 2016
Public Hearing	3rd Quarter 2015	4th Quarter 2015	2016

Appendices

Appendix A: Concept Paper for Rule 6-5: Fluidized Catalytic Cracking Units (FCCU)
Appendix B: Concept Paper for Changes to Rule 8-18: Equipment Leaks
Appendix C: Concept Paper for Changes to Rule 9-1: Refinery Fuel Gas Sulfur Limits
Appendix D: Concept Paper for Changes to Rule 9-1: Limiting SO_2 Emissions from Acid Plants
Appendix E: Concept Paper for Changes to Rule 11-10: Toxic and ROG emissions from Cooling Towers
Appendix F: Initial Proposal for Changes to Rule 9-9: Stationary Gas Turbines

Appendix C:
Concept Paper for Changes to Rule 9-1: Refinery Fuel Gas Sulfur Limits

Rules to Be Amended or Drafted

Regulation of refinery fuel gas (RFG) requires amendments to Air District Regulation 9, Rule 1, *Sulfur Dioxide*.

Goals

The goal of this rulemaking is to achieve technically feasible and cost-effective sulfur dioxide (SO_2) emission reductions from RFG systems at Bay Area refineries.

Background

The lightest components of crude oil separated by a refinery's atmospheric fractionator are methane and ethane, which are also the primary components of natural gas. At petroleum refineries, these products are not produced in marketable quantities, but are used as fuel in the numerous onsite steam generators and process heaters. When produced at a refinery, this product is called refinery fuel gas (RFG). Pipeline natural gas may be used as a supplemental fuel when needed to enhance the quality of RFG or when there is not enough RFG available. Unlike, pipeline natural gas, refinery fuel gas often contains significant quantities of sulfur that occur naturally in crude oil. When burned, these sulfur compounds are converted to SO_2.

Process and Source Description

RFG can contain between a few hundred and a few thousand parts per million-volume (ppmv) sulfur in the form of hydrogen sulfide (H_2S), carbonyl sulfide (COS), and organic sulfur compounds, such as mercaptans. During combustion, the sulfur in all of these compounds will oxidize to form SO_2, which is a criteria air pollutant and a precursor to particulate matter. Scrubbing with an amine or caustic solution can be effective at removing H_2S and some acidic sulfur containing compounds, but is generally ineffective at removing nonacidic sulfur compounds. Hydrotreating, a catalytic chemical process, converts these sulfur compounds to hydrogen sulfide which can then be removed by scrubbing.

All five Bay Area refineries maintain RFG collection and treatment systems. Four of the five refineries use a combination of hydrotreating and scrubbing to remove fuel sulfur from RFG; the Phillips 66 Refinery uses amine scrubbing alone.

Regulatory History and Context

On July 18, 1990, the Air District adopted Section 9-1-313.2, requiring all refineries that process more than 20,000 barrels per day of crude oil to operate a sulfur removal and recovery system that removes and recovers, on a refinery wide basis, 95 percent of the H_2S from RFG. The Rule does not specify an averaging period, test method, or monitoring criteria, but the Air District's Manual of Procedures does contain procedures for monitoring H_2S in RFG.

On March 15, 1978, U.S. Environmental Protection Agency (EPA) promulgated 40 CFR part 60, subpart J, *Standards of Performance for Petroleum Refineries (Subpart J)*. Subpart J applies to affected facilities at petroleum refineries that have been constructed or modified between June 11, 1973 and May 13, 2007.

Subpart J limits the H_2S content of RFG to 230 milligrams per dry standard cubic meter (mg/dscm). (40 CFR 60.104(a)(1))

On June 24, 2008, EPA promulgated 40 CFR part 60, subpart Ja, *Standards of Performance for Petroleum Refineries for which Construction, Reconstruction, or Modification Commenced after May 14, 2007 (Subpart Ja).* This regulation maintains the H_2S limit previously established in Subpart J, expressed as 162 parts per million by volume (ppmv) as a three hour rolling average. EPA allows an equivalent SO_2 emission limit from combustion units. (40 CFR 60.102a(g))

Review of the title V permits for the five Bay Area petroleum refineries did not reveal any facility-wide case-by-case fuel sulfur limits or SO_2 emission limit determinations for RFG in the Bay Area. There are a few limits that apply to individual pieces of equipment or subsets of equipment at individual refineries; but these vary regarding the species regulated (H_2S or total sulfur), the averaging period (24-hour up to 365-day rolling), and the numerical limit (45 ppmv up to 100 ppmv).

Emissions

The following table shows the magnitude of SO_2 emissions in pounds per day (rounded to the nearest hundred) from combustion of RFG:

Table C1: Refinery Fuel Gas SO_2 emissions

Facility	SO_2 Emissions from RFG Combustion (lb/day)
Chevron Products	500
Phillips 66	1,800
Shell Martinez	1,800
Tesoro Refining	300
Valero Refining	100
Total	**4,500**

Regulatory Concepts and Proposed Regulations

Air District staff identified regulatory concepts in two possible model regulations: EPA's *Standards of Performance for Petroleum Refineries* (40 CFR part 60, subparts J and Ja) and South Coast Air Quality Management District (SCAQMD) Rule 431.1, *Sulfur Content of Gaseous Fuels*.

1. U.S. EPA's *Standards of Performance for Petroleum Refineries (40 CFR part 60, subparts J and Ja)*

   The performance standards in these regulations that apply to RFG (limiting H_2S in RFG or SO_2 from combustion units) have already been discussed above.

   Refiners that chose to comply with the H_2S concentration limits are required to install, operate, calibrate, and maintain instruments that continuously monitor H_2S concentration in RFG prior to combustion. The subpart specifies performance standards, test methods, and quality assurance procedures for the monitor.

Similarly, if the refiner chooses to comply with the SO_2 emission limits, a continuous emission monitoring system (CEMS) is required and performance standards, test methods, and quality assurance procedures from 40 CFR part 60 are specified.

The regulations also contains the monitoring, recordkeeping, and reporting requirements typical of standards in part 60 that are easily incorporated into title V permits.

2. SCAQMD Rule 431.1 *Sulfur Content of Gaseous Fuels*

   SCAQMD limits the sulfur content of RFG, calculated as H_2S, to 40 ppmv, four-hour average. The initial compliance date was May 4, 1994 for large refineries and May 4, 1996 for small refineries. SCAQMD allows facilities to demonstrate equivalent SO_2 emission reductions within the facility, provided alternative plans have been approved by the Executive Officer in writing.

   Facilities burning gaseous fuels other than exclusively natural gas (e.g., RFG) are required to have continuous fuel gas monitoring systems (CFGMS) to determine the sulfur content of fuel prior to burning and upstream of mixing with natural gas, propane, or other fuels, or a CEMS to determine SO_2 emissions after burning. SCAQMD's requirements for CFGMS and CEMS, which are less detailed than EPA's performance standards, are included as an attachment to the Rule.

After reviewing these model rules, staff proposes limiting total fuel sulfur, as in SCAQMD's Rule 431.1, rather than H_2S, as in U.S. EPA's NSPS Ja, because all fuel sulfur oxidizes to SO_2 when burned.

Staff further proposes limiting RFG fuel sulfur to 40 ppmv. In November of 2010, SCAQMD prepared a report reviewing oxides of sulfur (SO_x) limits at several classes of emission units, including RFG systems, as part of its RECLAIM program. SCAQMD staff recommended retaining the 40 ppmv limit.

After reviewing Bay Area refinery RFG systems, staff found that four of the five refineries are already meeting this limit. However, staff recommends establishing a three-hour averaging period to be consistent with Volume V of the Air District's Manual of Procedures and 40 CFR subpart Ja

Thus, Air District staff is proposing:

1. <u>RFG Fuel Sulfur Limit:</u> 40 ppmv, three-hour average, measured as H_2S. Fuel sulfur is defined as the sum of hydrogen sulfide, carbonyl sulfide, and all other compounds that thermally oxidize to sulfur dioxide. At this time, an alternative SO_2 emission limit is not being proposed. Considering the large number of combustion units at the refineries and the difficulty related to monitoring them, an alternative SO_2 limit appears to be impractical.

2. <u>Proposed Monitoring Requirements:</u> Refiners must install, operate, calibrate, and maintain instruments that continuously monitor fuel sulfur concentration prior to combustion. Monitoring equipment shall comply with the Air District's Manual of Procedures.

Air District staff is also proposing a time frame of 24 months from promulgation of the rule until the initial compliance date to allow affected sources to obtain permits and install the necessary equipment.

Control Mechanisms

Staff expects that four of the five Bay Area refineries will be able to meet the RFG fuel sulfur limit with existing hydrotreating and scrubbing equipment. The Phillips 66 Refinery is expected to need a hydrotreating system for their RFG system.

Costs and Emissions Reductions

The four refineries already meeting the RFG fuel sulfur limit would not see any emissions reductions, but may incur some minor initial costs if their current fuel sulfur monitoring systems do not meet the requirements of the draft Rule.

Staff conservatively estimated that installation of a hydrotreating system at the Phillips 66 Refinery would cost approximately $20 million with about $1 million in operating costs. Phillips 66 reports average fuel sulfur concentration in RFG of 374.8 ppmv in the period from August 2010 until July 2013. A reduction to 40 ppmv results in the emission reduction in the following table.

Table C2: SO2 Emission Reductions and Control Costs

Facility	Emission Reduction (lbs/day)	Emission Reduction (tpy)	Total Annualized Cost ($)
Phillips 66	1594	291	$ 3,000,000